

# Charge transfer in the high dielectric constant materials $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$

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The cubic perovskite-related ceramic  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  has a very high static dielectric constant  $\epsilon_0 \gtrsim 10000$  at room temperature (RT), which drops to about 100 below  $\simeq 100$  K. Substituting Cd for Ca reduces the RT value of  $\epsilon_0$  by over an order of magnitude. The large  $\epsilon_0$  may be due to an internal barrier layer capacitance (IBLC) effect. Infrared optical properties show a low-frequency mode that increases dramatically in strength at low temperature, suggesting a change in the effective charges and a breakdown of the IBLC model due to a semiconductor-to-insulator transition.

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High dielectric constant materials find numerous technological applications. In the case of memory devices based on capacitive components, such as static and dynamic random access memories, the static dielectric constant  $\epsilon_0$  will ultimately decide the level of miniaturization. The dielectric constant of a material is related to the polarizability  $\alpha$ , in particular the dipole polarizability (an atomic property), which arises from structures with a permanent electric dipole which can change orientation in an applied electric field. These two quantities are linked through the Clausius-Mossotti relation. In insulators  $\epsilon_0 > 0$ ; materials with a dielectric constant greater than that of silicon nitride ( $\epsilon_0 > 7$ ) are classified as “high dielectric constant” materials. In general, a value of  $\epsilon_0$  above 1000 is related to either a ferroelectric which exhibits a dipole moment in the absence of an external electric field, or a relaxor characterized by a ferroelectric response under high electric fields at low temperature, but no macroscopic spontaneous polarization. However, both classes of materials show a peak in  $\epsilon_0$  as a function of temperature, which is undesirable for many applications. The body centered cubic (bcc) perovskite-related material  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  shown in Fig. 1 has recently attracted a great deal of attention due to its extremely high value for the static dielectric constant  $\epsilon_0 \sim 10^4$  measured in ceramics in the radio frequency (kHz) region [1, 2, 3], and was found to be practically constant in the 100 – 600 K region. Both properties are important for device implementation [4, 5]. However,  $\epsilon_0$  displays a 100-fold reduction below  $\sim 100$  K, without any detectable change in of the long-range crystallographic structure when probed by high-resolution x-ray [2] and neutron powder diffraction [1]. This contrasts with known ferroelectrics, which structurally distort because of soft-mode condensation [6, 7]. The substitution of Ca with Cd, results in a material with a similar temperature dependence, but a much lower dielectric constant,  $\epsilon_0 \sim 500$  in a ceramic [1]. Concerns have recently been raised that the large values for  $\epsilon_0$  is purely an extrin-

sic effect due to Maxwell-Wagner-type depletion layers at sample contacts or at grain boundaries [8]. However, recent measurements have been performed where the contacts were separated from the sample through the use of a thin aluminum oxide buffer layer; this showed that  $\epsilon_0 \sim 10^4$  for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  [9], ruling out contact contributions as the sole source of the large  $\epsilon_0$ . Moreover, it is not clear why the substitution of Cd for Ca results in such a dramatically lower value for  $\epsilon_0$ . In this letter, we present optical results which offer insights as to the origin of the large  $\epsilon_0$  in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  and its rapid decrease below  $\simeq 100$  K, as well as a possible explanation as to why  $\epsilon_0$  is much smaller in  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ .

Single crystals of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  were grown by the traveling-solvent floating-zone method with an image furnace using a technique that has been described in detail

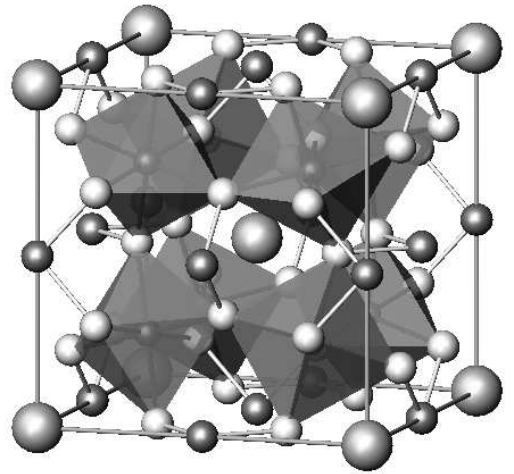


FIG. 1: The unit cell of body-centered cubic  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  in the  $Im\bar{3}$  space group. The Ti atoms sit at the center of the  $\text{TiO}_6$  octahedra, with bridging Cu atoms bonded to the oxygens, and large Ca atoms the corners and center of the unit cell.

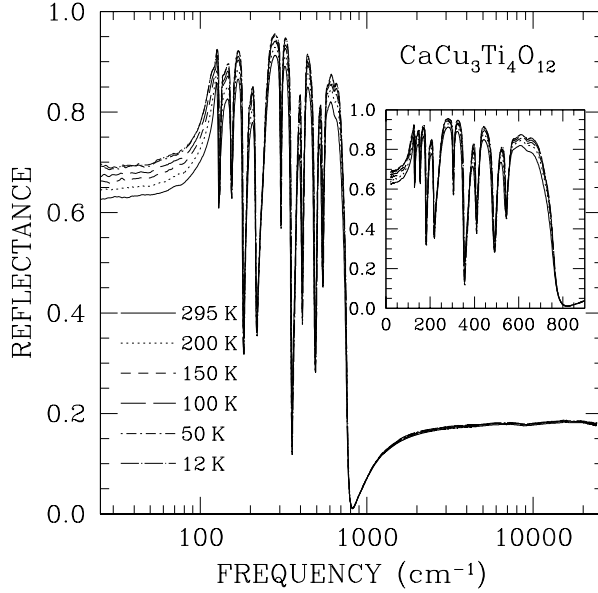


FIG. 2: The temperature dependence of the reflectance of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  from  $\approx 20$  to  $23\,000\text{ cm}^{-1}$ . The reflectance is typical for that of an insulator. Above highest longitudinal optic phonon frequency ( $\approx 700\text{ cm}^{-1}$ ), the reflectance becomes flat and featureless to the highest measured frequency, indicating that the gap edge has not yet been encountered (i.e.,  $2\Delta \gtrsim 3\text{ eV}$ ). Inset: The low-frequency reflectance.

elsewhere [3]. The ceramic compounds were prepared by conventional solid state reaction using starting oxides ( $\text{CaO}$  or  $\text{CdO}$ ,  $\text{TiO}_2$  and  $\text{CuO}$ ) with a purity of 99.9% or higher. The mixed powder taken in stoichiometric ratio was calcined at  $850^\circ\text{C}$  for 8 hours. The calcined powder was reground and pressed into disks and sintered in sealed gold tubes at  $1000^\circ\text{C}$  for 20 hours. X-ray diffraction data showed the materials are a single-phase. The  $\text{ACu}_3\text{Ti}_4\text{O}_{12}$  family of compounds has been known for some time [10], and their structures have been determined (Fig. 1).

The temperature dependent reflectance of polished  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (crystal) and  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$  (ceramic) have been measured over a wide range ( $\approx 20$  to  $23\,000\text{ cm}^{-1}$ ) using an overcoating technique [11]. In practice, the reflectance of ceramics and crystals is nearly identical. The reflectance of the Ca material shown in Fig. 2 is typical of a non-metallic system. The sharp features in the reflectance are due to the unscreened infrared active lattice vibrations; above the highest observed phonon frequency the reflectance is flat and featureless up to the highest measured frequency, suggesting that the optical value for the optical gap  $2\Delta \gtrsim 3\text{ eV}$ . The optical properties have been determined from a Kramers-Kronig analysis of the reflectance, which requires extrapolations at high and low frequencies. At low frequency, the reflectance was assumed to be constant below the

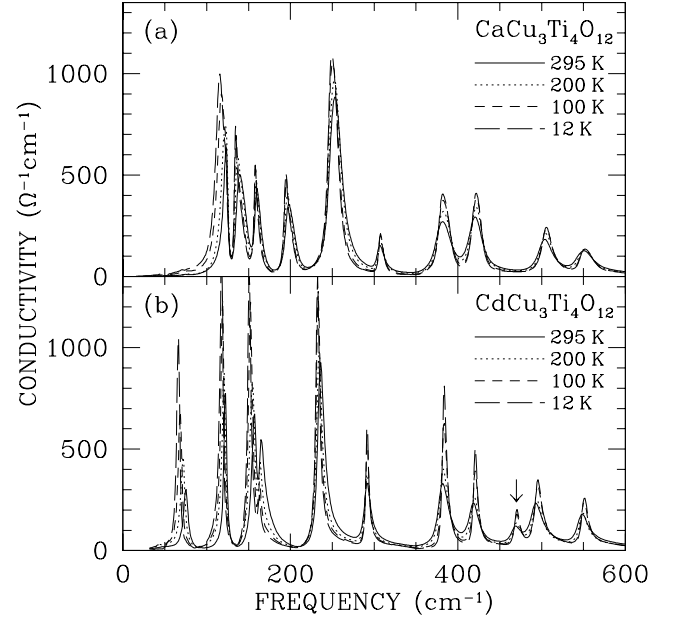


FIG. 3: (a) The temperature dependent optical conductivity of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ . The low-frequency infrared-active lattice modes soften and show an anomalous increase in oscillator strength with decreasing temperature. (b) The temperature dependent optical conductivity of  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ . The low-frequency modes show the same anomalous increase in strength with decreasing frequency, and in addition, many of the vibrations in this material are narrower at low temperature. Note the unusual appearance of a new mode at  $\sim 470\text{ cm}^{-1}$  (arrow) in the Cd material. (The vibrational parameters are tabulated in Table I.)

lowest measured frequency for  $\omega \rightarrow 0$ , while at high frequency the reflectance was assumed to be constant above the highest measured point to  $2 \times 10^5\text{ cm}^{-1}$ , above which a free-electron approximation ( $R \propto \omega^{-4}$ ) was assumed.

The real part of the optical conductivity, derived from the imaginary part of the dielectric function  $\sigma_1 = \omega\epsilon_2/4\pi$ , is shown for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  in Fig. 3(a) in the low frequency region. As with the reflectance, the conductivity is characteristic of a semiconductor or insulator [ $\sigma_{dc} \equiv \sigma_1(\omega \rightarrow 0) \approx 0$ ], and is dominated by the lattice modes. The low-frequency modes display an anomalous increase in oscillator strength at low temperature. The optical conductivity of  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$  is shown in Fig. 3(b). The low frequency vibrations in the Cd material have the same anomalous increase in strength at low temperature. In addition, a new mode is clearly observed at  $\approx 470\text{ cm}^{-1}$ ; this mode is curiously absent in the Ca material [3, 12], and will be discussed in more detail in a future work. Below  $\approx 300\text{ cm}^{-1}$ , there are some significant downward frequency shifts with doping with respect to the Ca material, indicating that Cd (Ca) plays a significant role in these vibrations. The infrared active modes have been fitted using the complex dielec-

TABLE I: The phonon parameters for Lorentzian fits to the conductivity of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  and  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$  at 10 and 295 K, where  $\omega_j$ ,  $\gamma_j$  and  $\omega_{p,j}$  are the frequency, width and effective plasma frequency of the  $j$ th vibration. All units are in  $\text{cm}^{-1}$ .

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}^a$						$\text{CdCu}_3\text{Ti}_4\text{O}_{12}^b$					
295 K			10 K			295 K			10 K		
$\omega_j$	$\gamma_j$	$\omega_{p,j}$	$\omega_j$	$\gamma_j$	$\omega_{p,j}$	$\omega_j$	$\gamma_j$	$\omega_{p,j}$	$\omega_j$	$\gamma_j$	$\omega_{p,j}$
552	27	435	554	18	376	550	26	484	552	13	421
504	19	445	506	14	454	494	20	500	497	13	502
—	—	—	—	—	—	468	13	250	471	7.1	277
421	19	553	422	11	529	419	17	450	421	6.1	421
382	18	535	383	13	560	383	15	533	384	6.0	534
308	8.7	255	308	5.2	246	292	13	471	292	4.8	410
254	16	913	251	12	916	237	10	745	233	5.8	681
199	9.9	456	195	7.1	448	166	13	575	163	8.0	291
161	7.8	423	159	5.2	388	156	5.6	433	151	4.7	619
141	11	562	136	6.1	453	122	4.0	434	118	4.6	636
122	6.0	464	116	12	851	75	6.9	348	66	4.3	523

<sup>a</sup>Single crystal and ceramic samples yield similar results.

<sup>b</sup>Ceramic results only.

tric function  $\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$  for Lorentz oscillators

$$\tilde{\epsilon}(\omega) = \epsilon_\infty + \sum_j \frac{\omega_{p,j}^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j}, \quad (1)$$

where  $\omega_j$ ,  $\gamma_j$  and  $\omega_{p,j}$  are the frequency, width and effective plasma frequency of the  $j$ th vibration;  $\epsilon_\infty$  is the core contribution to the dielectric function at high frequencies. The results of the fits to the conductivity are shown in Table I at 10 and 295 K for both materials.

The anomalous increase in oscillator strength of the low frequency modes is unusual, and has important consequences. Optical sum rules provide a powerful tool with which to analyze the behavior of free carriers and bound excitations [13]. The partial conductivity sum rule for oscillators states that [14]

$$\frac{120}{\pi} \int_{\omega_a}^{\omega_b} \sigma_1(\omega) d\omega = \omega_{p,j}^2, \quad (2)$$

where the interval  $\omega_a \rightarrow \omega_b$  is chosen so that the full spectral weight of the  $j$ th oscillator is captured. In the absence of changes in the bonding or coordination, the mode may narrow with decreasing temperature, but the spectral weight (proportional to area under the peak, or  $\omega_{p,j}^2$ ) should not change. The dramatic increase in the oscillator strength of the low-frequency mode (Fig. 3 and Table I) is a clear violation of this sum rule, which in turn has implications for the distribution of charge within the unit cell. Light couples to the induced dipole moments created by the atomic displacements associated with a normal mode — if the Born effective charge per atom  $Z^*$  is increasing, then the size of the induced dipole moment and the optical absorption will also increase. For a material with  $k$  atoms in the unit cell, the effective charge

per atom can be defined as [15]

$$\frac{1}{\epsilon_\infty} \sum_j \omega_{p,j}^2 = \frac{4\pi}{V_c} \sum_k \frac{(Z_k^* e)^2}{M_k} \quad (3)$$

where  $\sum_k Z_k^* = 0$ ,  $V_c$  is the unit cell volume, and  $j$  and  $k$  index the lattice modes and the atoms with mass  $M_k$ , respectively. The fitted values of  $\omega_{p,j}$  in Table I indicate that there is an increase between room temperature and 10 K in the left side of Eq. 3 of  $\simeq 11\%$  in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ , and  $\simeq 4\%$  in  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ . The increase in the left side of Eq. 3 implies that the  $Z_k^*$ 's are increasing with decreasing temperature. In oxide materials, oxygen is often the lightest element, so that the summation is dropped and the change in the effective charge is associated purely with the oxygen (i.e.,  $Z_k^* \equiv Z_{\text{O}}^*$ ). While the presence of other light elements in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  may complicate this approach, it is less of a problem in the Cd material. The deduced values for  $Z_{\text{O}}^*$  are shown in Fig. 4, and illustrate a noticeably different behavior for the Ca and Cd materials. While Cd is somewhat smaller ( $\sim 16\%$ ) than the Ca cation, the main difference between these two materials is their electronegativity, or the ability of an atom to attract electrons to itself. The Pauling electronegativity for Ca and Cd are 1.0 and 1.7, respectively. It is expected that an atom with a higher electron affinity will result in less charge transfer to the oxygen atoms, and the reduction in  $Z_{\text{O}}^*$  is precisely what is in fact observed in the Cd material.

The large dielectric constant observed in these materials must ultimately be due to either intrinsic effects that arise from the properties of the material, or extrinsic effects, such as contact problems [8]. However, the persistence of the large value of  $\epsilon_0$  with the addition of a buffer layer between the sample and the contact indicates that contact problems alone are not the source of the large dielectric constant. On the other hand, the absence of a structural transition tends to rule out the possibility that the large  $\epsilon_0$  is the result of intrinsic effects, such as the displacements of Ca atoms or some distortion that involves the  $\text{TiO}_6$  octahedra. A more compelling explanation comes from the observation that  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is heavily twinned [1]. Recent results based on impedance spectroscopy on  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  ceramics indicate that these materials may be understood as being semiconducting regions separated by insulating barriers, and that the giant dielectric phenomena is attributed to an internal barrier layer capacitance (IBLC) effect [16]. The IBLC results in a large  $\epsilon_0$  that has the same Debye-like frequency dependence that has been observed in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  [2, 3]. However, one of the more puzzling aspects of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ , and to a lesser extent  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ , is the rapid suppression of  $\epsilon_0$  at low temperature. The large values for  $\epsilon_0$  have been shown to persist in thin films [17], and transport measurements of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  thin films shown in the inset of Fig. 4 indi-

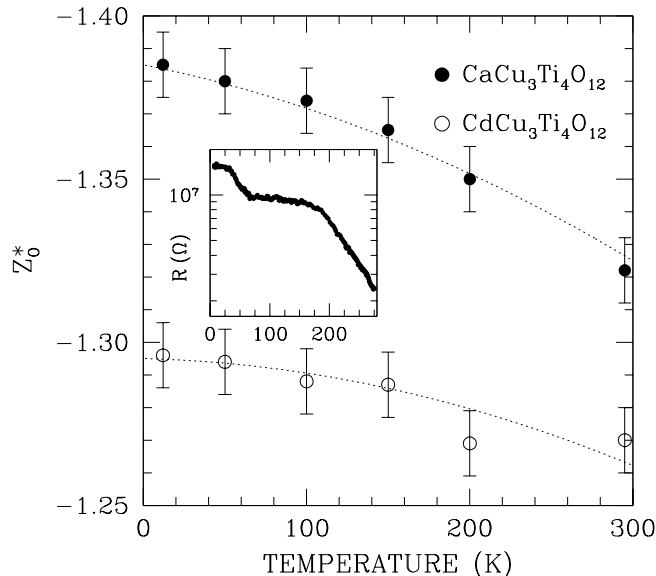


FIG. 4: The temperature dependence of the deduced values Born effective charge per oxygen atom ( $Z_O^*$ ) in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  and  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ . The dotted lines are drawn as a guide to the eye. Note that the value for  $Z_O^*$  in the Cd material is lower for the Ca material, and that the  $Z_O^*$  increases by more than 5% in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ , compared to an increase of less than 2% in  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ . Inset: The temperature dependence of the resistance of a thin film of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ . The resistance increases with decreasing temperature, but there is a discontinuity close to 100 K.

cate that there is an anomaly in the resistance at  $\sim 100$  K that is suggestive of a semiconductor-to-insulator (SI) transition; such a transition would result in the rapid expansion of the insulating domains in the IBLC picture and a commensurate reduction of  $\epsilon_0$ . Furthermore, the SI transition is consistent with the observation of the increasing degree of ionicity within the unit cell of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ . The lower value of  $\epsilon_0$  in  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$  suggests that the material is not as heavily twinned, which may in turn be related to the slightly lower values of  $Z_O^*$  in this material.

In summary, the optical properties of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  and  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$  have been measured at a variety of temperatures. A low frequency mode is observed to strengthen dramatically at low temperature, indicating that the Born effective charges are increasing in the unit cell. We propose that the large  $\epsilon_0$  may be due to extrinsic mechanisms such as the formation of boundary-layer

capacitors, and that the rapid reduction of  $\epsilon_0$  at low temperature is due to an SI transition and the removal of an IBLC mechanism. The  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$  system may have a lower value of  $\epsilon_0$  due to a reduced degree of twinning.

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